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**CRYSTAL FIELD AND MAGNETIC PROPERTIES OF  $\text{ErH}_3$**

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# CRYSTAL FIELD AND MAGNETIC PROPERTIES OF $\text{ErH}_3$

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## ABSTRACT

Magnetization and magnetic susceptibility measurements have been made in the temperature range 1.3 to 4.2 K on powdered samples of  $\text{ErH}_3$ . The susceptibility exhibits Curie-Weiss behavior from 4.2 to 2 K, and intercepts the negative temperature axis at  $\theta = 1.05 \pm 0.05$  K, indicating that the material is antiferromagnetic. The low field effective moment is  $6.77 \pm 0.27$  Bohr magnetons per ion. The magnetization exhibits a temperature independent contribution, the slope of which is  $(5 \pm 1.2) \times 10^{-6}$  Weber m/kg Tesla. The saturation moment is  $3.84 \pm 0.15$  Bohr magnetons per ion. The results can be qualitatively explained by the effects of crystal fields on the magnetic ions. No definitive assignment of a crystal field ground state can be given, nor can a clear choice between cubically or hexagonally symmetric crystal fields be made. For hexagonal symmetry, the first excited state is estimated to be 86 to 100 K above the ground state. For cubic symmetry, the splitting is on the order of 160 to 180 K.

## INTRODUCTION

Hydrogen in a rare earth lattice affects the magnetic properties of the host material in at least two ways: (1) by altering the exchange mechanism; (2) by producing crystalline electric fields at the rare earth sites. Wallace and co-workers [1, 2] have shown that the ordering temperature of rare earth hydrides decreases with increasing hydrogen concentration. Since the interaction which produces ordering

in the rare earths is indirect exchange, anything which depletes the conduction band should weaken the exchange and lower the ordering temperature. Wallace, et al., concluded that hydrogen must reside in the lattice as an anion. Additional evidence confirming the anionic nature of hydrogen in the rare earth host can be obtained from an investigation of the effects of crystalline electric fields on the magnetic properties of the material.

The general form of the crystal field Hamiltonian is

$$H_{CF} = \sum_{\ell, m} B_{\ell}^m O_{\ell}^m \quad (1)$$

where the  $O_{\ell}^m$  are Steven's operator equivalents [3], and the  $B_{\ell}^m$  are expansion coefficients, and depend on the symmetry of the charges producing the crystal field. The crystal field energy levels are described by the parameters  $W$  and  $x$ , defined by

$$Wx = B_4^0 F_4 \quad (2)$$

and

$$W(1 - |x|) = B_6^0 F_6 \quad (3)$$

where  $F_4$  and  $F_6$  are positive numerical factors, and  $B_4^0$  and  $B_6^0$  are lattice sums related to the 4th order and 6th order terms in the crystal field Hamiltonian. The algebraic signs of  $W$  and  $x$  are determined by  $B_4^0$  and  $B_6^0$ , which in turn depend on the sign of the charges producing the crystal fields. Lea, Leask and Wolfe [4] have found the signs of  $B_4^0$ ,  $B_6^0$ ,  $W$ , and  $x$  for cubic symmetry, and Segal and Wallace [5] have found them for hexagonal symmetry. The results are shown in Table I. The crystal field ground states corresponding to the signs of  $W$  and  $x$  in Table I are listed in Table II. The notation is that of Lea, Leask, and Wolfe (cubic) and Segal and Wallace (hexagonal). Figures 1 and 2 are the energy level diagrams in each case.

## EXPERIMENTAL

The magnetization  $\sigma$  was detected by sweeping an externally applied field and integrating the induced emf from two search coils wound in series-opposition. One coil contained the sample, while the other was empty. Measurements were made in fields ranging to 10 Teslas, and at temperatures from 2.2 to 4.2 K. Standard field modulation techniques were employed to measure susceptibility,  $\chi$ , as a function of temperature over the range 1.3 to 4.2 K. The samples were commercially prepared powders of  $\text{ErH}_3$ , and were kept in 4 mm i.d. by 100 mm glass tubes sealed with a ground glass stopper. The total mass and average density were determined to within 0.1%. The uncertainties in the relative values of  $\chi$  were typically 0.5%, and of magnetization, 3%.

## RESULTS

The inverse a.c. magnetic susceptibility of  $\text{ErH}_3$  as a function of temperature is shown in Fig. 3 for the temperature range 4.2 to 1.3 K. The inverse susceptibility exhibits Curie-Weiss behavior from 4.2 K to at least 2 K. Extrapolation from the Curie-Weiss region to the negative temperature axis yields  $\theta_N = (1.05 \pm 0.05)\text{K}$  for the Curie-Weiss constant. The data appear to deviate systematically from the Curie-Weiss extrapolation below approximately 1.8 K. The low-field effective moment,  $p_{\text{eff}} = g_J J(J+1)^{1/2}$ , determined from the slope of the straight line in Fig. 3, is  $6.77 \pm 0.27$  Bohr magnetons per ion. The free-ion value is  $9.58 \mu_B$ . Kubota and Wallace, [2], on the basis of measurements of  $\chi$  vs.  $T$  up to room temperatures, reported  $9.54 \mu_B$  per ion. The difference arises because several crystal field levels will be significantly populated at room temperature.

The isothermal magnetization is shown as a function of applied field for several temperatures in Fig. 4. The approach to saturation and the zero high-field slope are clearly evident. The slope of the temperature independent contribution to  $\sigma$  is  $(5.0 \pm 1.2) \times 10^{-6}$  Weber m/kg Tesla.



The saturation magnetization,  $\sigma_{\text{sat}}$ , is  $(1.58 \pm 0.06) \times 10^{-4}$  Weber m/kg. The latter quantity is obtained by linearly extrapolating from the high-field region to  $B = 0$ , where the temperature independent moment vanishes. Since

$$\sigma_{\text{sat}} = N_o g_p J \mu_B / M \quad (4)$$

the saturation moment per ion is  $g_p J = (3.84 \pm 0.15) \mu_B$ , where  $g_p$  is the Lande factor appropriate to a powdered sample,  $M$  is the gram molecular mass,

## DISCUSSION

The observed values of the effective moment and saturation moment are consistent with the assumption that the ground state is an isotropic Kramer's doublet. In such a case the low field data yield  $g_p = (2/\sqrt{3}) p_{\text{eff}} = 7.8 \pm 0.3$ , while the high field data give  $g_p = 2\sigma_{\text{sat}} M / N_o \mu_B = 7.7 \pm 0.3$ , in good agreement with one another. The values from the two field regions would disagree markedly if the material were strongly anisotropic. If the symmetry of the crystalline electric field is cubic (or nearly cubic), then the allowed ground states for the anionic model are  $\Gamma_6$  and  $\Gamma_7$  (see Fig. 1). A protonic model is virtually ruled out in this instance, since the ground state would be  $\Gamma_8(3)$ , an anisotropic quartet of levels. For hexagonally symmetric crystal fields the possible ground states for the hydridic model are those labeled a and g in Fig. 2  $\Gamma_7(\pm 1/2)$  and  $\Gamma_7(\pm 13/2)$ . According to S&W [5] these two states have isotropic magnetic moments at  $x = -0.04$ . None of the other states listed in Table II are isotropic for any value of  $x$  in the range  $-1 \leq x \leq 0$ . Similarly, none of the allowable states in the protonic model possess an isotropic ground state magnetic moment, and are therefore all ruled out.

Numerical estimates of the splitting between the ground state and first excited state can be made by first computing  $\langle J_z \rangle$  and  $\langle J_x \rangle$  using the wave functions (or estimates of them) provided by Lea, Leask, and

Wolfe, and Segal and Wallace, and then calculating the temperature independent contribution to the susceptibility, given by [6]

$$\chi_p = \frac{432\pi}{\Delta} \left\{ \frac{|\langle J_z \rangle|^2}{3} + \frac{2|\langle J_x \rangle|^2}{3} \right\} \quad (5)$$

where  $\Delta$  is the energy difference between the states in question. At  $x = -1$  in Fig. 1,  $\Delta_{6-8} \approx 180$  K, and is approximately constant in the range  $-1 \leq x \leq -0.6$ . For  $-0.4 \leq x \leq 0$ ,  $\Delta_{7-8} \approx 160$  K. No estimate can be easily made for the range  $-0.6 \leq x \leq -0.4$ , since  $\Delta$  varies rapidly between  $\Gamma_8$  and both  $\Gamma_6$  and  $\Gamma_7$  in this range. ( $\Delta_{6-8}$  and  $\Delta_{7-8}$  are still the appropriate splittings to calculate in this range, since  $\langle J_z \rangle = \langle J_x \rangle = 0$  between  $\Gamma_6$  and  $\Gamma_7$  for all values of  $x$ .) For hexagonal crystal fields with  $\Gamma_7(\pm 13/2)$  as the ground state, the available expressions for the wave functions at  $x = 0$  can be used. The result is  $\Delta \approx 86$  K. Approximate values for the coefficients in the expression for  $\Gamma_7(\pm 1/2)$  were found by trial and error and used with the expression for  $\Gamma_7(\pm 13/2)$  at  $x = 0$  to calculate the splitting between  $\Gamma_7(\pm 1/2)$  as the ground state and  $\Gamma_7(\pm 13/2)$ , with the result that  $\Delta \approx 100$  K.

Calculated values of the slope of the temperature dependent part of the inverse susceptibility are all in substantial disagreement with the experimental value. For cubic symmetry, the calculated values are  $\sim 32\%$  too large for  $\Gamma_7$  and  $\sim 70\%$  too large for  $\Gamma_6$ . For hexagonal symmetry, both choices for ground state predict values of  $d(1/\chi_p)/dT$  that are  $\sim 32\%$  too large.

## CONCLUSION

The data are consistent with the assumption that the ground state is an isotropic Kramer's doublet, but no definitive assignment of a crystal field ground state can be made. If the crystal fields possess cubic (or nearly cubic) symmetry, the energy difference between the

ground state and first excited state is  $\sim 160$  to  $180$  K. If the crystal fields are more nearly hexagonal, the splitting is on the order of  $86$  to  $100$  K. In both cases, the evidence supports an assumption that the hydrogen exists in the rare earth lattice as a negatively charged ion (anionic model).

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TABLE I. - ALGEBRAIC SIGNS FOR CRYSTAL  
FIELD PARAMETERS FOR  $J = 15/2$

Coordination	$H^-$				$H^+$			
	$B_4^O$	$B_6^C$	W	x	$B_4^O$	$B_6^O$	W	x
Cubic	-	+	+	-	+	-	-	-
Hexagonal	-	+	+	-	+	-	-	-

TABLE II. - CRYSTAL FIELD GROUND STATES FOR  $J = 15/2$

Coordination	$H^-$	$H^+$
Cubic	$\Gamma_6, \Gamma_7$	$\Gamma_8(3)$
Hexagonal	$\Gamma_9(\pm 15/2), \Gamma_7(\pm 1/2), \Gamma_7(\pm 13/2)$	$\Gamma_7(\pm 11/2), \Gamma_9(\pm 9/2), \Gamma_8(\pm 7/2)$

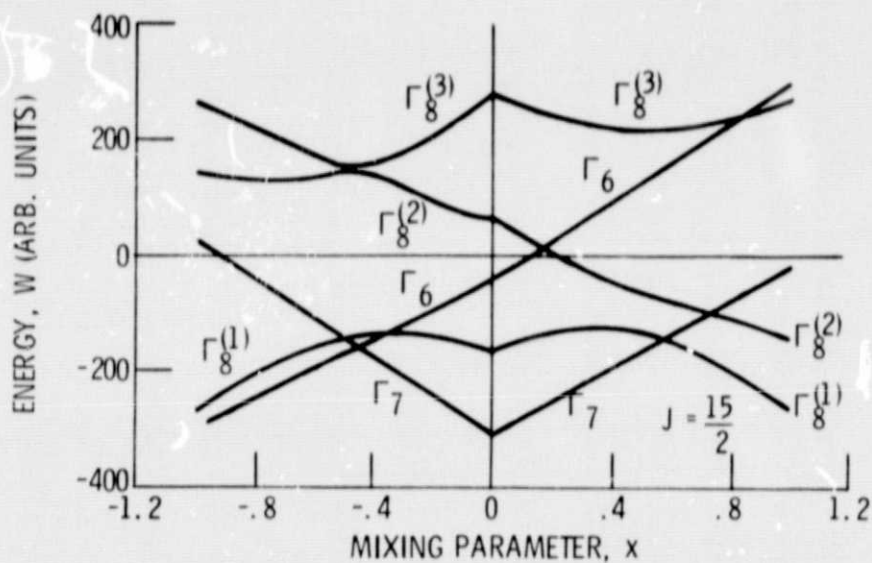


Figure 1. - Energy level diagram for  $\text{Er}^{3+}$  ( $J = 15/2$ ) after LLW (ref. 8) for cubic symmetry. The ordinate is the crystal field splitting parameter  $W$ . The abscissa is  $x$ , the 4th order to 6th order mixing parameter.

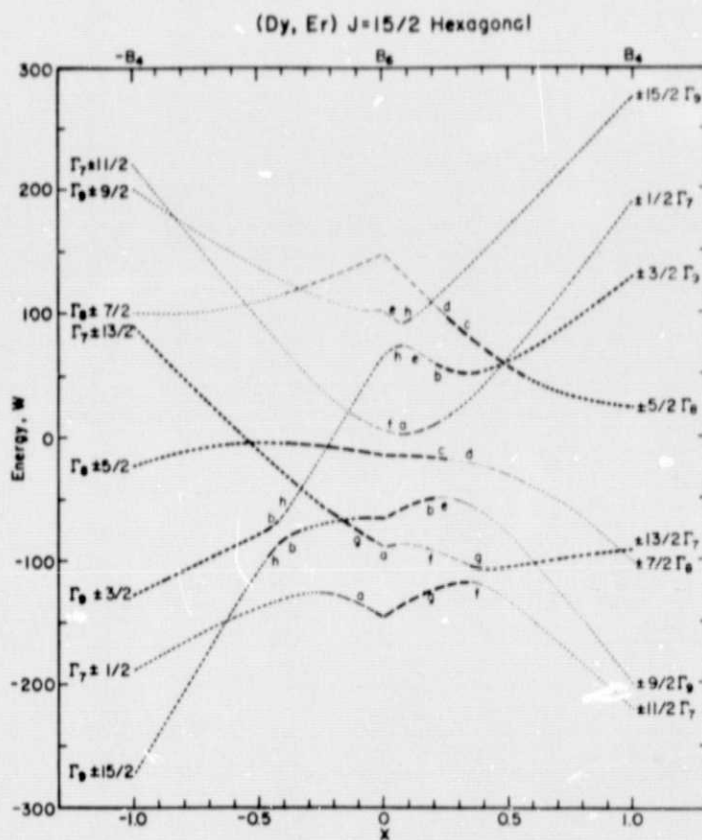


Figure 2. - Energy level diagram for  $\text{Er}^{3+}$  ( $J = 15/2$ ) after S&W (ref. 9) for hexagonal symmetry. The ordinate is the crystal field splitting parameter  $W$ . The abscissa is  $x$ , the 4th order to 6th order mixing parameter.

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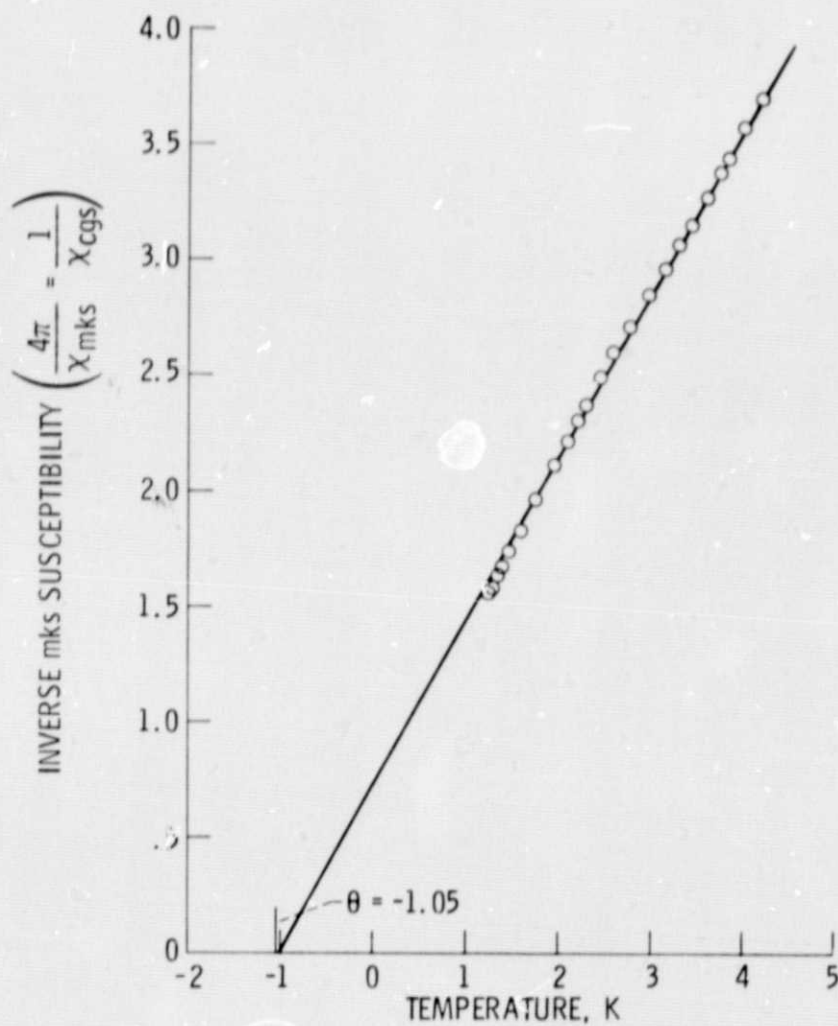


Figure 3. - Inverse differential susceptibility of  $\text{ErH}_3$  versus temperature.

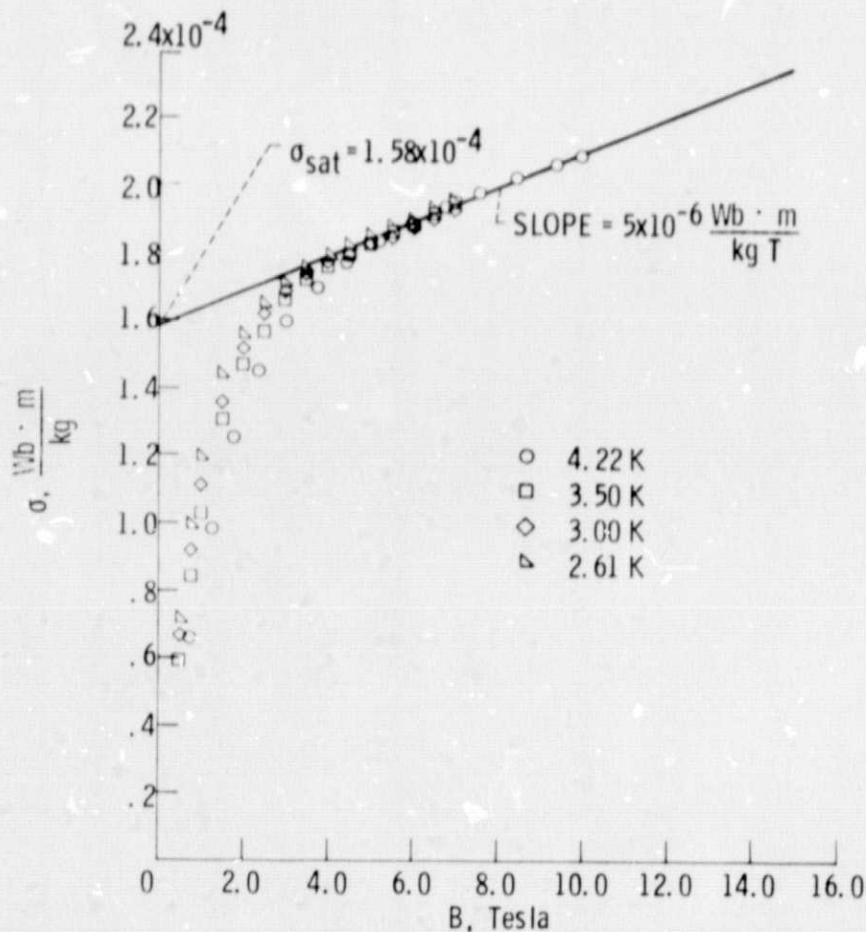


Figure 4. - Magnetization of  $\text{ErH}_3$  versus applied magnetic induction.